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Gas analysis — General quality aspects and metrological traceability of calibration gas mixtures

Analyse des gaz — Aspects généraux sur la qualité et traçabilité des mélanges de gaz pour étalonnage

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 158, *Analysis of gases*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

This first edition of ISO 14167 cancels and replaces ISO/TS 14167:2003, which has been technically revised. The main changes compared to the previous edition are as follows:

- the description of quality assurance aspects has been improved;
- the relationship between ISO/TC 158 standards has been described;
- the metrological traceability and metrological hierarchy of calibration gas mixtures has been elaborated upon.

Gas analysis — General quality aspects and metrological traceability of calibration gas mixtures

1 Scope

This document provides requirements and guidelines on the necessary quality assurance required to produce calibration gas mixtures that are demonstrably stable and comparable. It shows that this is achieved by demonstrating that the composition of the calibration gas mixture is metrologically traceable to the SI.

This document shows that calibration gas mixtures can be prepared according to methods that have measurements that are completely described in SI units. It describes procedures for verifying that the composition of such gas mixtures is correct within the stated measurement uncertainty. Guidance is given as to how to conduct the evaluation of uncertainty in these procedures.

This document also shows how a calibration gas mixture with unknown composition can be calibrated by reference to traceable standard gas mixtures.

This document covers the commonalities and differences of quality management schemes in use by producers of calibration gas mixtures, most notably those described in ISO/IEC 17025 and ISO 17034. These systems lead to gas mixtures with different characteristics, and this document explains these differences and their implications.

Calibration gas mixtures, as prepared and certified for composition in accordance with this document, are used for the calibration of equipment, the performance evaluation of methods, measurement procedures and equipment.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO Guide 30, *Reference materials — Selected terms and definitions*

ISO/IEC Guide 98-3, *Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)*

ISO/IEC Guide 98-3/Suppl 1, *Supplement 1 to the Guide to the expression of uncertainty in measurement — Propagation of distributions using a Monte Carlo method*

ISO/IEC Guide 98-3/Suppl 2, *Supplement 2 to the Guide to the expression of uncertainty in measurement — Extension to any number of output quantities*

ISO/IEC Guide 99, *International vocabulary of metrology — Basic and general concepts and associated terms (VIM)*

ISO 6142 (all parts), *Gas analysis — Preparation of calibration gas mixtures*

ISO 6143, *Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures*

ISO 6144, *Gas analysis — Preparation of calibration gas mixtures — Static volumetric method*

ISO 6145-1, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 1: Methods of calibration*

ISO 6145-2, *Gas analysis — Preparation of calibration gas mixtures using dynamic methods — Part 2: Piston pumps*

ISO 6145-4, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 4: Continuous syringe injection method*

ISO 6145-5, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 5: Capillary calibration devices*

ISO 6145-6, *Gas analysis — Preparation of calibration gas mixtures using dynamic methods — Part 6: Critical flow orifices*

ISO 6145-7, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 7: Thermal mass-flow controllers*

ISO 6145-8, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 8: Diffusion method*

ISO 6145-9, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 9: Saturation method*

ISO 6145-10, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 10: Permeation method*

ISO 6145-11, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 11: Electrochemical generation*

ISO 7504, *Gas analysis — Vocabulary*

ISO 12963, *Gas analysis — Comparison methods for the determination of the composition of gas mixtures based on one- and two-point calibration*

ISO 14912, *Gas analysis — Conversion of gas mixture composition data*

ISO 16664, *Gas analysis — Handling of calibration gases and gas mixtures — Guidelines*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 7504, ISO Guide 30 and ISO/IEC Guide 99 apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

4 Symbols

i,k	indices for components in a gas or gas mixture
j	index for a parent gas
M	molar mass
m	mass
q_m	mass flow rate
n	amount of substance

q_n amount-of-substance flow rate

p pressure

q number of components in the gas mixture

R ideal gas constant

r number of parent gases

T temperature

V volume

q_V volume flow rate

v mass fraction of a component in a parent gas

w mass fraction of a component in a gas mixture

x amount-of-substance fraction of a component in a parent gas

y amount-of-substance fraction of a component in a gas mixture

Z compressibility factor

φ volume fraction of a component in a parent gas

ϕ volume fraction of a component in a gas mixture

5 Preparation of gas mixtures

5.1 Static and dynamic methods

Gas mixtures can be prepared using either static or dynamic methods. Static methods mix portions of gas, dynamic methods mix flows of gas. These portions are commonly quantified as masses (gravimetric methods) or volumes (volumetric methods).

Static methods lead to the preparation of a calibration gas mixture in a cylinder, and are generally used for components that are stable in cylinders. Static methods can be gravimetric [covered in ISO 6142 (all parts)] or volumetric (covered in ISO 6144). These methods are employed to produce compressed calibration gas mixtures in cylinders. High-pressure gas mixtures are usually prepared gravimetrically. The volumetric method of ISO 6144 is commonly used in connection with a vessel (gas mixing chamber) and operated at lower pressures, but still well above ambient pressure. The filling pressure is determined by the request of the customer and limited by the physical properties of the gas mixture, more specifically the condensation behaviour. Static gravimetric preparation of calibration gas mixtures shall be done in accordance with ISO 6142 (all parts). For the static volumetric preparation of calibration gas mixtures, ISO 6144 shall be used.

Dynamic methods are described by the ISO 6145 series. These methods are based on the principle that mixing gases with constant flow rates leads to a gas mixture with a defined composition. The appropriate part(s) of ISO 6145 shall be used for the dynamic preparation of calibration gas mixtures.

Both types of methods have their strengths and weaknesses. The most suitable preparation method is determined based on the constituents and the composition of the desired gas mixture, and the practical circumstances of use, among other factors.

Some producers use a manometric method to prepare a calibration gas mixture of a specified composition. Such gas mixtures can be characterized to become calibration gas mixtures using a comparison method as described in Clause 6.

5.2 Purity of parent gases

The composition of parent gases plays a role in gas mixture preparation. It is not always necessary to perform a rigorous purity analysis, neither is it always acceptable to compute the composition of calibration gas mixtures while ignoring the effects of impurities. In ISO 19229, criteria are given regarding to what extent purity analysis is required. These shall be followed both in static and dynamic gas mixture preparation. The resulting purity data can be expressed in different forms, of which the amount-of-substance and volume fractions are the most commonly used. Dynamic gravimetric methods often require the use of purity data expressed in mass fractions. As necessary, purity data shall be converted using the appropriate conversion method as described in ISO 14912.

5.3 Use of gas mixtures as parent gases

Most of the written standards for gas mixture preparation, such as ISO 6142 (all parts), ISO 6144 and the ISO 6145 series, describe methods for working with pure gases. These methods are, however, also applied for preparing calibration gas mixtures using other gas mixtures as parent gases. Although this use is not always formally covered by the scope of the International Standards mentioned above, it is common practice in the entire gas analysis area. The rationale behind this use is that there are practical limitations with respect to the dilution factors that can be achieved with the desired accuracy for the various methods.

Complex multicomponent calibration gas mixtures, such as synthetic natural gas mixtures and stack gas mixtures, are practically always prepared using a multistage preparation process. The expressions used for computing composition, as summarized in 5.4 and 5.5, are also valid for calibration gas mixtures prepared from a combination of pure gases and gas mixtures.

5.4 Gravimetric methods

In gravimetric gas mixture preparation, the masses of the transferred parent gases (or liquids) are recorded. When using pure materials, the composition can directly be calculated from the masses of the parent gases *j*, which are in this case identical to the masses of the components *i*. The mass fraction of a component *k* is computed as:

$$w_k = \frac{m_k}{\sum_{i=1}^{q} m_i} \quad (1)$$

If the molar composition is desired, by using the molar masses of the components *i*, the amount-of-substance fraction of a component *k* is computed as:

$$y_k = \frac{m_k / M_k}{\sum_{i=1}^{q} m_i / M_i} \quad (2)$$

It is important to recognize that the amount-of-substance of a component *k* is computed as $n_k = m_k / M_k$.

Both Formula (1) and Formula (2) underline the primary character of gravimetric methods: the composition can be calculated from first principles, without the need to refer to measurement standards of the same kind, that is, the use of calibration gas mixtures or other standards characterized for composition.

In practice however, the formulae are insufficient for an accurate computation of the composition of the prepared gas mixture, because the materials used for producing the mixture are not pure. To deal with the impurities, all parent gases (and liquids) shall be considered as mixtures themselves. The methods for purity analysis (see ISO 19229) as well as those for characterizing the composition of the gas mixtures used can involve the use of measurement standards of the same kind, thus compromising the primary character of the preparation method. The appreciation of the composition of the parent gases (or liquids) leads to expressions that are much more complex than Formulae (1) and (2).

The mass fraction of a component k is now computed by calculating the mass of component k across all parent gases and dividing this mass by the total mass of the mixture:

$$w_k = \frac{\sum_{j=1}^{r} m_j v_{k,j}}{\sum_{j=1}^{r} m_j} \tag{3}$$

where $v_{k,j}$ denotes the mass fraction of component k in parent gas j.

Similarly, the composition expressed in amount-of-substance fractions can be computed while appreciating the composition of the parent gases. The expression for the amount-of-substance fraction of a component k in the gas mixture is computed as:

$$y_k = \frac{\sum_{j=1}^{r} \left(\frac{x_{k,j} m_j}{\sum_{i=1}^{q} x_{i,j} M_i} \right)}{\sum_{j=1}^{r} \left(\frac{m_j}{\sum_{i=1}^{q} x_{i,j} M_i} \right)} \tag{4}$$

This expression is well known from ISO 6142-1. A derivation of this expression is given in this document. The numerator of Formula (4) equals the amount-of-substance of component k, whereas the denominator equals the total amount-of-substance of the mixture.

Formulae (3) and (4) are widely used in gas metrology. They not only apply to gas mixtures prepared from pure gases, but can also be used for gas mixtures prepared from other gas mixtures.

Dynamic gravimetric methods shall be employed using the same models as the static methods, where the masses are replaced by the corresponding mass flow rates. The molar composition of a dynamically prepared gas mixture shall be computed from:

$$y_k = \frac{\sum_{j=1}^{r} \left(\frac{x_{k,j} (q_m)_j}{\sum_{i=1}^{q} x_{i,j} M_i} \right)}{\sum_{j=1}^{r} \left(\frac{(q_m)_j}{\sum_{i=1}^{q} x_{i,j} M_i} \right)} \tag{5}$$

Formula (5) differs from Formula (4) only in that it takes the mass flow rates rather than the masses to compute the composition. A prerequisite for the validity of using Formula (5) is that the mass flow rates are constant within a narrow range, the width of which determines the measurement uncertainty.

NOTE Formula (3) can be reworked in a similar manner to apply to dynamic methods.

5.5 Volumetric methods

In volumetric gas mixture preparation, the volumes of the transferred parent gases (or liquids) are recorded. When using pure materials, the composition can be directly calculated from the volumes of the parent gases j, which are in this case identical to the volumes of the components i. The volume fraction of a component k is calculated as:

$$\phi_k = \frac{V_k}{\sum_{i=1}^{q} V_i} \tag{6}$$

provided that the temperature and pressure of all parent gases are the same.

Similar to the case of gravimetric methods, the amount-of-substance can be computed from the gas volumes. The amount-of-substance of component k shall be computed as:

$$n_k = \frac{p_k V_k}{R T_k} \tag{7}$$

assuming that the gas is an ideal gas. The amount-of-substance fraction of component k is computed as:

$$y_k = \frac{n_k}{\sum_{i=1}^{q} n_i} \tag{8}$$

where the amount-of-substance is computed using Formula (7).

Formulae (6) and (8) underline the primary character of volumetric methods: the composition can be calculated from first principles, without the need to refer to measurement standards of the same kind, that is, the use of calibration gas mixtures or other standards characterized for composition.

In practice, however, Formulae (6) and (8) are insufficient for an accurate computation of the composition of the prepared gas mixture, because the materials used for producing the mixture are not pure. To deal with the impurities, all parent gases (and liquid) shall be considered as mixtures themselves. The methods for purity analysis (see ISO 19229), as well as those for characterizing the composition of the gas mixtures used, can involve the use of measurement standards of the same kind, thus compromising the primary character of the preparation method.

A further issue that specifically applies to the volumetric methods is that for an accurate composition the parent gases need to be considered as *real gases*, which means that the conversion of volume to amount-of-substance shall take into account the compressibility factor of the parent gas. Formula (7) thus becomes:

$$n_k = \frac{p_k V_k}{R T_k Z_k} \tag{9}$$

The compressibility factor, Z, is a function of the temperature, pressure and composition. Valid methods for computing the compressibility factor are given in, among others, ISO 14912. Equations-of-state can also be used for this purpose.